

19



Europäisches Patentamt  
European Patent Office  
Office européen des brevets

11 Publication number:

0 063 880  
A1

12

# EUROPEAN PATENT APPLICATION

21 Application number: 82301812.2

51 Int. Cl.: C 08 G 69/44

22 Date of filing: 06.04.82

30 Priority: 06.04.81 US 251625

71 Applicant: CELANESE CORPORATION, 1211 Avenue Of  
The Americas, New York New York 10036 (US)

43 Date of publication of application: 03.11.82  
Bulletin 82/44

72 Inventor: Charbonneau, Larry F., 166 Lafayette Avenue,  
Chatham New Jersey (US)  
Inventor: Calundann, Gordon W., 1275 Rock Avenue,  
North Plainfield New Jersey (US)  
Inventor: East, Anthony J., 62 Niles Avenue, Madison  
New Jersey (US)

84 Designated Contracting States: BE DE FR GB IT NL

74 Representative: De Minvielle-Devaux, Ian Benedict  
Peter et al, CARPMAELS & RANSFORD 43, Bloomsbury  
Square, London WC1A 2RA (GB)

54 Poly(esteramide) derived from 6-hydroxy-2-hydroxy naphthoic acid.

57 A melt processable poly(ester-amide) which is capable of forming an anisotropic melt phase is provided. The poly(ester-amide) of the present invention consists essentially of the recurring units (a) 6-oxy-2-naphthoyl moiety, (b) aromatic moiety capable of forming an amide linkage in the polymer and, optionally, (c) other aromatic moiety derived from aromatic hydroxyacid, in the proportions indicated. The aromatic moiety capable of forming an amide linkage in the polymer is an amino derivative or a substituted amino derivative of an aromatic carboxylic acid. Preferably, the aromatic moiety capable of forming an amide linkage is derived from p-aminobenzoic acid. The resulting poly(ester-amide) exhibits a melting temperature below 400°C., preferably below 350°C. The poly(ester-amide) of the present invention is preferably formed by a melt polymerisation technique.

Best Available Copy

EP 0 063 880 A1

ACTORUM AG

# TITLE MODIFIED

see front page

1

0063880

Poly(ester-amide) capable of forming an anisotropic melt phase derived from 6-hydroxy-2-naphthoic acid, aromatic monomer capable of forming an amide linkage and other aromatic hydroxyacid.

The present invention provides a poly(ester-amide) derived from 6-hydroxy-2-naphthoic acid, another aromatic hydroxyacid, and aromatic monomer capable of forming an amide linkage. The poly(ester-amide) is preferably  
5 wholly aromatic. The poly(ester-amide) is melt processable and is capable of forming an anisotropic melt phase.

The invention also provides fibres, films, moulding compounds and moulded articles based thereon.

The use of objects moulded from synthetic polymers has  
10 expanded rapidly in recent decades. In particular, polyesters and polyamides have widely gained acceptance for general moulding applications and in the formation of fibres and films. An additional class of polymers known as poly(ester-amides) has been disclosed. Such disclosures include  
15 U.S. Patents Nos. 2,547,113; 2,946,769; 3,272,774; 3,272,776; 3,440,218; 3,475,385; 3,538,058; 3,546,178; 3,575,928; 3,676,291; 3,865,792; 3,926,923 and 4,116,943. Polyimide esters are disclosed in German Offenlegungsschrift (DOS) 2,950,939 and in U.S. Patent No. 4,176,223.

20 Although many polyesters, polyamides and poly(ester-amides) have mechanical properties suitable for general applications, most polyesters, polyamides and poly(ester-amides) are not suitable for high strength service because the mechanical properties are not sufficiently high. One  
25 group of polymers that are suitable for high strength service without the use of a reinforcing agent is a new class of polymers exhibiting a general overall balance of mechanical properties substantially enhanced over previous polymers. These polymers have been described by various terms,  
30 including "liquid crystalline", "liquid crystal", "thermotropic", "mesogenic" and "anisotropic". Briefly, the polymers of this new class are thought to involve a parallel ordering of the molecular chains. The state wherein the

BAD ORIGINAL



molecules are so ordered is often referred to either as the liquid crystal state or the nematic phase of the liquid crystal state. These polymers are prepared from monomers which are generally long, flat and fairly rigid along the long axis of the molecule and commonly have chain extending linkages that are either coaxial or parallel.

Disclosures of polyesters which exhibit melt anisotropy include (a) Polyester X76-A Self Reinforced Thermoplastic, by W. J. Jackson, Jr., H.F. Kuhfuss and T.F. Gray, Jr., 30th Anniversary Technical Conference, 1975 Reinforced Plastics/Composites Institute, The Society of the Plastics Industry, Inc., Section 17-D, Pages 1 to 4, (b) Belgian Patents 828,935 and 828,936, (c) Dutch Patent 7505551, (d) West German Patents 2520819, 2520820, 2722120, 2834535, 2834536 and 2834537, (e) Japanese Patents 43-223; 2132-116; 3017-692 and 3021-293, (f) U.S. Patents 3,991,013; 3,991,014; 4,057,597; 4,066,620; 4,067,852; 4,075,262; 4,083,829; 4,093,595; 4,118,372; 4,130,545; 4,130,702; 4,146,702; 4,153,779; 4,156,070; 4,159,365; 4,161,470; 4,169,933; 4,181,792; 4,183,895; 4,184,996; 4,188,476; 4,201,856; 4,219,461; 4,224,433; 4,228,218; 4,230,817; 4,232,143; 4,232,144; 4,238,598; 4,238,599; 4,245,082 and 4,245,084, and (g) U.K. published Applications 2,002,404; 2,008,598 and 2,030,158. Other such materials are discussed in U.S. Serial Nos. 54,049, filed July 2, 1979; 91,003, filed November 5, 1979; 109,573, filed January 4, 1980; 109,575, filed January 4, 1980; 128,759, filed March 10, 1980; 128,778, filed March 10, 1980 and 169,014, filed July 15, 1980. (USSN 169,014 corresponds to European Patent Application 81303161.4, published as 44205).

Representative disclosures of liquid crystalline polyamide dopes include U.S. Patents 3,673,143; 3,748,299; 3,767,756; 3,801,528; 3,804,791; 3,817,941; 3,819,587; 3,827,998; 3,836,498; 4,016,236; 4,018,735; 4,148,774 and Reissue 30,352.

U.S. Patent No. 4,182,842 discloses poly(ester-amides) prepared from an aromatic dicarboxylic acid, ethylene



glycol and a p-acylaminobenzoic acid. Such poly(ester-amides) are also disclosed in "Liquid Crystal Polymers. III. Preparation and Properties of Poly(Ester-Amides) from p-Aminobenzoic Acid and Poly(Ethylene Terephthalate)", by W.J. Jackson, Jr. and H.F. Kuhfuss, J. Appl. Polym. Sci., Vol. 25, No. 8, pp 1685-94 (1980). A similar disclosure is Japanese 54 125271. These references neither disclose nor suggest the poly(ester-amide) of the present invention.

European Patent Application No. 79301276.6 (Publication No. 0 007 715) discloses melt processable fibre-forming poly(ester-amides) comprising residues of one or more amino-phenols selected from p-aminophenol and p-N-methylamino-phenol and residues of one or more dicarboxylic acids. The poly(ester-amide) contains a balance of linear difunctional residues and dissymmetric difunctional residues derived from either the aminophenols or the acids. The linear difunctional residues and dissymmetric difunctional residues are chosen so as to give a product which melts below its decomposition temperature and exhibits optical anisotropy in the melt. This Patent neither discloses nor suggests the poly(ester-amide) of the present invention which contains a 6-oxy-2-naphthoyl moiety.

U.S. Patent No. 3,859,251 discloses a poly(ester-amide) which comprises a dicarboxyl moiety which comprises 50 to 100 mole percent of units derived from an acyclic aliphatic dicarboxylic acid. Such units are not required in the poly(ester-amide) of the present invention. Moreover, while the Patent discloses the inclusion of a p-oxybenzoyl moiety, there is no disclosure nor suggestion of the usefulness of a poly(ester-amide) containing a 6-oxy-2-naphthoyl moiety, such as that of the present invention.

U.S. Patent No. 3,809,679 discloses poly(ester-amides) consisting of 10 to 90 mole percent of recurring structural units derived from a dicarboxylic acid dihalide and a dihydroxy compound of a specified formula and 10 to 90 mole percent of recurring structural units derived from a dicarboxylic acid dihalide and a diamino compound of a specified formula. The poly(ester-amides) specifically



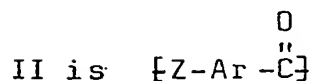
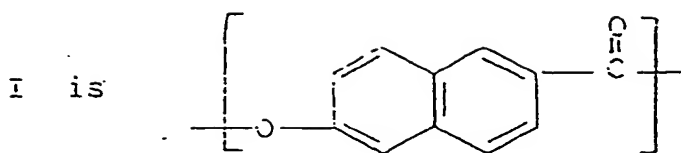
exclude moieties derived from aromatic hydroxyacids, such as the 6-oxy-2-naphthoyl moiety included in the poly(ester-amide) of the present invention. Furthermore, most, if not all, of the poly(ester-amides) disclosed are not readily melt processable, and there is no disclosure of the existence of an anisotropic melt phase.

Our U.S. Applications Serial Nos. 214,557, filed December, 9, 1980, entitled "Poly(ester-amide) Capable of Forming an Anisotropic Melt Phase Derived from 6-Hydroxy-2-Naphthoic Acid, Dicarboxylic Acid, and Aromatic Monomer Capable of Forming an Amide Linkage" (Inventors: Anthony J. East, Larry F. Charbonneau, and Gordon W. Calundann), and 251,629 filed April 6, 1981, entitled "Poly(ester-amides) Capable of Forming an Anisotropic Melt Phase Derived From 6-Hydroxy-2-Naphthoic Acid, Other Aromatic Hydroxyacid, Carbocyclic Dicarboxylic Acid, and Aromatic Monomer Capable of Forming an Amide Linkage" (Inventors: Larry F. Charbonneau, Anthony J. East, and Gordon W. Calundann), relate to melt processable poly(ester-amides) exhibiting anisotropy in the melt phase which include an oxynaphthoyl moiety. Unlike the present invention, the poly(ester-amides) there described include an additional moiety derived from a carbocyclic dicarboxylic acid. Furthermore, the amide-forming moieties there disclosed do not include a carboxylic functional group, as does the amide-forming moiety employed in the present invention. However, despite such structural differences, the poly(ester-amide) of the present invention likewise demonstrates anisotropy and excellent tractability in the melt phase.

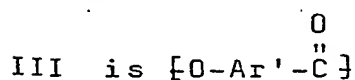
It is an object of the present invention to provide an improved poly(ester-amide) which is suited for the formation of quality moulded articles, melt extruded fibres and melt extruded films.

The invention provides a melt processable poly(ester-amide) capable of forming an anisotropic melt phase at a temperature below 400°C. consisting essentially of the recurring moieties I, II and (optionally) III wherein:





where Ar is a divalent radical comprising at least one aromatic ring, and Z is NH or NR (where R is an alkyl group of 1 to 6 carbon atoms or an aryl group); and



where Ar' is a divalent radical comprising at least one aromatic ring other than naphthylene;

10 wherein at least some of the hydrogen atoms present upon any of the rings in the various moieties may optionally be replaced by substituents selected from alkyl groups of 1 to 4 carbon atoms, alkoxy groups of 1 to 4 carbon atoms, halogen, phenyl and mixtures thereof,

15 and wherein moiety I is present in a concentration of 10 to 90 mole percent, moiety II is present in a concentration of 5 to 45 mole percent and moiety III is present in a concentration of 0 to 45 mole percent, the total concentration of moieties I and III being from 55 to 95 mole percent.

20 By means of the present invention there is provided an improved poly(ester-amide) which forms a highly tractable melt phase.

This improved poly(ester-amide) forms an anisotropic melt phase at a temperature well below its decomposition  
25 temperature and can be used to produce fibres, films and moulded articles of high quality.

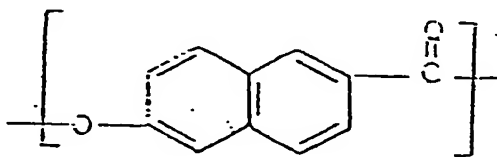
By means of the invention it is possible to obtain an improved melt processable poly(ester-amide) capable of forming an anisotropic melt phase at a temperature below  
30 400°C., and preferably below 350°C.

The improved melt processable poly(ester-amide) exhibits improved adhesion, improved fatigue resistance and increased transverse strength.

The poly(ester-amide) of the present invention includes at least two recurring moieties which when combined in the poly(ester-amide) in the above proportions have been found to form an atypical, optically anisotropic melt phase. The polymer forms an anisotropic melt phase at a temperature below 400°C. (e.g. below 350°C.). The polymer melting temperatures may be confirmed by the use of a differential scanning calorimeter (DSC) employing repeat scans at a 20°C. per minute heat-up rate and by observing the peak of the DSC melt transition. The poly(ester-amide) commonly exhibits a melting temperature of at least 200°C. and preferably of at least 250°C. as determined by differential scanning calorimetry. The poly(ester-amide) of the present invention may exhibit more than one DSC transition temperature.

Because of its ability to exhibit anisotropic properties (i.e., liquid crystalline properties) in the melt, the poly(ester-amide) readily can form a product having a highly oriented molecular structure upon melt processing. Preferred poly(ester-amide) compositions are capable of undergoing melt processing at a temperature within the range of 250°C. to 350°C., as discussed more fully hereinafter.

The poly(ester-amide) includes two essential moieties. Moiety I can be termed a 6-oxy-2-naphthoyl moiety and possesses the structural formula:



While not specifically illustrated in the structural formula, at least some of the hydrogen atoms present upon the aromatic rings of moiety I may be substituted. Representative ring substituted compounds from which moiety I can be derived.

include: 6-hydroxy-5-chloro-2-naphthoic acid, 6-hydroxy-5-methyl-2-naphthoic acid, 6-hydroxy-5-methoxy-2-naphthoic acid, 6-hydroxy-7-chloro-2-naphthoic acid and 6-hydroxy-5,7-dichloro-2-naphthoic acid. The presence of ring substitution tends to modify to some degree the physical properties of the resulting polymer (e.g., the polymer may soften at a lower temperature, its impact strength may be improved and the crystallinity of the solid polymer may be decreased). In a preferred embodiment wherein a poly(ester-amide) of optimum crystallinity in the solid state is desired, no ring substitution is present.

As will be apparent to those skilled in the art, moiety I can be derived from unsubstituted 6-hydroxy-2-naphthoic acid and the derivatives thereof. A convenient laboratory preparation for forming 6-hydroxy-2-naphthoic acid is described in Berichte, Vol. 58, 2835-45 (1925) by K. Fries and K. Schimmelschmidt. Also, U.S. Patent No. 1,593,816 is concerned with a process for synthesizing 6-hydroxy-2-naphthoic acid by reacting carbon dioxide with the potassium salt of beta-naphthol.

Moiety I is present in the poly(ester-amide) of the present invention in a concentration of 10 to 90 mole percent. Preferably, moiety I is present in a concentration within the range of 20 to 80 mole percent, and, more preferably, within the range of 30 to 70 mole percent.

The second essential moiety (i.e., moiety II) is derived from a monomer which is capable of forming an amide linkage in the polymer. Moiety II possesses the structural formula



where Ar is a divalent radical comprising at least one aromatic ring, and Z is NH or NR, where R is an alkyl group of 1 to 6 carbon atoms or an aryl group. R is preferably a straight-chain alkyl group of 1 to 6 carbon atoms and is more preferably a methyl group.

Moiety II is an aminocarboxyaryl moiety, wherein the amino group may be substituted or unsubstituted. Examples of



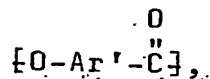
monomers from which moiety II can be derived include p-amino-benzoic acid, p-N-methylaminobenzoic acid, m-aminobenzoic acid, 3-methyl-4-aminobenzoic acid, 2-chloro-4-aminobenzoic acid, 4-amino-1-naphthoic acid, 4-N-methylamino-1-naphthoic acid, 4-amino-4'-carboxydiphenyl, 4-amino-4'-carboxydiphenyl ether, 4-amino-4'-carboxydiphenyl sulfone, 4-amino-4'-carboxydiphenyl sulfide and p-aminocinnamic acid.

Preferably moiety II is a symmetrical aminocarboxyaryl moiety. By "symmetrical" is meant that the divalent bonds which join the moiety to other moieties in the main polymer chain are symmetrically disposed on one or more rings (e.g., are para to each other or diagonally disposed, for example, on the 2,6 positions when present on a naphthalene ring). This definition can also be expressed as follows: there is an axis of symmetry at right angles to the plane of the molecule. The preferred moiety which may serve as a symmetrical aminocarboxyaryl moiety in the poly(ester-amide) of the present invention is a moiety derived from p-aminobenzoic acid. An example of a non-symmetrical aminocarboxyaryl moiety is one derived from m-aminobenzoic acid.

Although moiety II may be substituted in the same manner as moiety I, highly satisfactory polymers can be formed wherein the aminocarboxyaryl moiety is free of ring substitution.

Moiety II is present in the poly(ester-amide) in a concentration of 5 to 45 mole percent, preferably in a concentration of 5 to 35 mole percent. In an especially preferred embodiment, moiety II is present in a concentration within the range of 10 to 30 mole percent.

In addition to the two essential moieties described above, the poly(ester-amide) may further include an additional moiety (moiety III). Moiety III is derived from an aromatic hydroxyacid other than 6-hydroxy-2-naphthoic acid or derivatives thereof. Moiety III has the structural formula



where "Ar'" is a divalent radical comprising at least one

aromatic ring other than naphthylene. Moiety III is preferably derived from a symmetrical aromatic hydroxyacid. By "symmetrical" is meant that the divalent bonds which join the moiety to other moieties in the main polymer chain are  
5 symmetrically disposed on one or more rings (e.g., are para to each other or diagonally disposed when present in a condensed ring system). This definition can also be expressed as follows: there is an axis of symmetry at right angles to the plane of the molecule.

- 10 The preferred moiety which may serve as a symmetrical aromatic moiety derived from a hydroxyacid is a p-oxybenzoyl moiety.

Although moiety III may be substituted in the same manner as moiety I, highly satisfactory polymers can be  
15 formed wherein moiety III is free of ring substitution.

Other aromatic hydroxyacids from which moiety III may be derived include 4-hydroxycinnamic acid and 4-hydroxy-3-methoxycinnamic acid (ferulic acid).

Moiety III is present in the poly(ester-amide) of the  
20 present invention in a concentration of 0 to 45 mole percent. Preferably, moiety III is present in a concentration of at least 5 mole percent and more preferably in a concentration of at least 10 mole percent. For example, in a preferred embodiment, moiety III may be present in a concentration  
25 within the range of 5 to 45 mole percent and, in a more preferred embodiment, within the range of 10 to 30 mole percent.

The total concentration of moieties I and III is within the range of 55 to 95 mole percent. Preferably, the total  
30 molar concentration of moieties I and III is within the range of 65 to 95 mole percent. In an especially preferred embodiment, the total concentration of moieties I and III is within the range of 70 to 90 mole percent.

As stated above, the poly(ester-amide) of the present  
35 invention may consist essentially of 10 to 90 mole percent of moiety I, 5 to 45 mole percent of moiety II and 0 to 45 mole percent of moiety III. Preferred compositions consist essentially of 20 to 80 mole percent of moiety I, 5 to 35

mole percent of moiety II and 5 to 45 mole percent of moiety III. Even more preferred are those compositions which consist essentially of 30 to 70 mole percent of moiety I, 10 to 30 mole percent of moiety II and 10 to 30 mole percent of moiety III.

The various moieties upon polymer formation will tend to be present in a random configuration.

If substituents are present on the rings of each of the moieties described above, they are selected from alkyl groups of 1 to 4 carbon atoms, alkoxy groups of 1 to 4 carbon atoms, halogen and phenyl (and mixtures of the foregoing).

Other ester-forming moieties (e.g., dicarboxy, dioxy or hydroxycarboxy units) other than those previously discussed may be additionally included in the poly(ester-amide) of the present invention (normally in a minor concentration) so long as such moieties do not adversely influence the desired anisotropic melt phase exhibited by the poly(ester-amide) heretofore defined and do not raise the melting temperature of the resulting polymer above 400°C.

The poly(ester-amide) of the present invention commonly

exhibits  $-O-\overset{\overset{O}{\parallel}}{C}-CH_3$ ,  $-\overset{\overset{O}{\parallel}}{C}-OH$ ,  $-\overset{\overset{O}{\parallel}}{C}-NH-$ , or  $-\overset{\overset{O}{\parallel}}{C}-CH_3$  end groups depending upon the synthesis route selected. As will be apparent to those skilled in the art, the end groups optionally may be capped, e.g., acidic end groups may be capped with a variety of alcohols, and hydroxyl end groups may be capped with a variety of organic acids. For instance, end capping units such as phenyl ester ( $-\overset{\overset{O}{\parallel}}{C}-O-\text{C}_6\text{H}_5$ ) and

methyl ester ( $-\overset{\overset{O}{\parallel}}{C}-O-CH_3$ ) optionally may be included at the end of the polymer chains. The polymer also may be oxidatively cross-linked to at least some degree, if desired, by heating in an oxygen-containing atmosphere (e.g. in air) while in bulk form or as a previously shaped article at a temperature below its melting temperature for a limited period of time (e.g., for a few minutes).

The poly(ester-amide) of the present invention tends to be substantially insoluble in all common solvents, such as hexafluoroisopropanol and o-chlorophenol, and accordingly is not susceptible to solution processing. It can surprisingly be readily processed by common melt processing techniques as discussed hereafter. Most compositions are soluble to some degree in pentafluorophenol.

The poly(ester-amide) of the present invention commonly exhibits a weight average molecular weight (as prepared) of 5,000 to 50,000, and preferably 10,000 to 30,000, e.g., 15,000 to 17,500. Such molecular weight may be determined by standard techniques not involving the solutioning of the polymer, e.g., by end group determination via infrared spectroscopy on compression moulded films. Alternatively, light scattering techniques in a pentafluorophenol solution may be employed to determine the molecular weight.

The poly(ester-amide) of the present invention is capable of undergoing melt processing at a temperature within the range of 200°C. to 400°C. Preferably, the polymer is melt processed at a temperature within the range of 250°C. to 350°C. and more preferably within the range of 270°C. to 330°C.

The melting temperature ( $T_m$ ) of the poly(ester-amide) of the present invention may vary widely with the composition of the poly(ester-amide).

The poly(ester-amide) prior to heat treatment additionally commonly exhibits an inherent viscosity (i.e. I.V.) of at least 1.0 dl./g., and preferably at least 2.0 dl./g., when measured at a concentration of 0.1 weight/volume percent in pentafluorophenol at 60°C.

The poly(ester-amide) of the present invention commonly may be considered crystalline in the sense that fibres melt extruded therefrom exhibit X-ray diffraction patterns characteristic of polymeric crystalline materials, using Ni filtered CuK  $\alpha$  radiation and flat plate cameras. In those embodiments wherein ring substitution is present, as previously described, the polyesters may be substantially less



crystalline in the solid phase and exhibit diffraction patterns typical of oriented amorphous fibres. In spite of the crystallinity commonly observed, the poly(ester-amide) of the present invention nevertheless may be easily melt processed in all instances.

The poly(ester-amide) of the present invention is readily tractable and forms an anisotropic melt phase whereby an atypical degree of order is manifest in the molten polymer. The improved tractability of the present poly(ester-amide) is due, at least in part, to the presence of moiety I, i.e., the 6-oxy-2-naphthoyl moiety. It has been observed that the tractability of the polymer is a function of the molar concentration of moiety I in the polymer.

The subject poly(ester-amide) readily forms liquid crystals in the melt phase. Such anisotropic properties are manifest at a temperature which is amenable for melt processing to form shaped articles. Such order in the melt may be confirmed by conventional polarised light techniques whereby crossed polarisers are utilised. More specifically, the anisotropic melt phase may conveniently be confirmed by the use of a Leitz polarising microscope at a magnification of 40X with the sample on a Leitz hot stage and under a nitrogen atmosphere. The polymer melt is optically anisotropic, i.e., it transmits light when examined between crossed polarisers. Light is transmitted when the sample is optically anisotropic even in the static state.

The poly(ester-amide) of the present invention may be formed by a variety of techniques whereby organic monomer compounds possessing functional groups which upon condensation form the requisite recurring moieties are reacted. For instance, the functional groups of the organic monomer compounds may be carboxylic acid groups, hydroxyl groups, ester groups, acyloxy groups, acid halides, amine groups or acetamide groups. The organic monomer compounds may be reacted in the absence of a heat-exchange fluid via a melt acidolysis procedure. They accordingly may be heated initially to form a melt solution of the reactants with the reaction continuing as solid polymer particles are formed and suspended therein.

A vacuum may be applied to facilitate removal of volatiles formed during the final stage of the condensation (e.g. acetic acid or water). Such a technique is disclosed in European Patent Application No. 79301276.6 (Publication No 5 0 007.715).

In our United States Patent No. 4,067,852 entitled "Improved Melt Processable Thermotropic Wholly Aromatic Polyester and Process for Its Production", is described a slurry polymerisation process which, although directed to 10 the production of wholly aromatic polyesters, may be employed to form the poly(ester-amide) of the present invention. In that process, the solid product is suspended in a heat exchange medium.

When employing either the melt acidolysis procedure or 15 the slurry procedure of United States Patent No. 4,067,852, the organic monomer reactants from which the hydroxyacid moieties (i.e., moieties I and III) are derived may be initially provided in a modified form whereby the usual hydroxyl groups of these monomers are esterified (i.e., they 20 are provided as acyl esters). For instance, lower acyl esters of 6-hydroxy-2-naphthoic acid wherein the hydroxyl group is esterified may be provided as reactants. The lower acyl groups preferably have from 2 to 4 carbon atoms. Preferably, the acetate esters of the organic compounds which form 25 moieties I and III are provided. In addition, the amine group of moiety II may be provided as a lower acyl amide. Accordingly, particularly preferred reactants for the condensation reaction include 6-acetoxy-2-naphthoic acid, p-acetoxybenzoic acid and p-acetamidobenzoic acid.

30 Representative catalysts which optionally may be employed in either the melt acidolysis procedure or in the procedure of United States Patent No. 4,067,852 include alkyl tin oxide (e.g., dibutyl tin oxide), diaryl tin oxide, alkyl tin acids, acyl esters of tin, titanium dioxide, alkoxy titanium 35 silicates, titanium alkoxides, alkali and alkaline earth metal salts of carboxylic acids (e.g., sodium acetate), the gaseous acid catalysts such as Lewis acids (e.g.,  $\text{BF}_3$ ),



hydrogen halides (e.g. HCl), etc. The quantity of catalyst utilised typically is 0.001 to 1 percent by weight based upon the total monomer weight, and most commonly 0.01 to 0.12 percent by weight.

5 The molecular weight of a previously formed polyester may be further increased via a solid state polymerisation procedure wherein the particulate polymer is heated in a flowing inert gaseous atmosphere (e.g., in a flowing nitrogen atmosphere) at a temperature approximately 20°C. below the  
10 melting temperature of the polymer for 10 to 12 hours.

The poly(ester-amide) of the present invention readily can be melt processed to form a variety of shaped articles, e.g., moulded three-dimensional articles, fibres, films, tapes, etc. The poly(ester-amide) of the present invention  
15 is suited for moulding applications and may be moulded via standard injection moulding techniques commonly utilised when forming moulded articles. It is not essential that more severe moulding conditions (e.g., higher temperatures, compression moulding, impact moulding or plasma spraying  
20 techniques) be utilised. Fibres or films may be melt extruded.

A moulding compound may be formed from the poly(ester-amide) of the present invention which incorporates 1 to 60 percent by weight of a solid filler (e.g., talc) and/or  
25 reinforcing agent (e.g., glass fibres).

The poly(ester-amide) also may be employed as a coating material which is applied as a powder or from a liquid dispersion.

When forming fibres and films, the extrusion orifice  
30 may be selected from among those commonly utilised during the melt extrusion of such shaped articles. For instance, the shaped extrusion orifice may be in the form of a rectangular slit (i.e., a slit die) when forming a polymeric film. When forming a filamentary material, the spinneret  
35 selected may contain one and preferably a plurality of extrusion orifices. For instance, a standard conical



spinneret, such as those commonly used in the melt spinning of polyethylene terephthalate, containing 1 to 2000 holes (e.g., 6 to 1500 holes) having a diameter of 1 to 60 mils (0.0254 to 1.524 mm) (e.g., 5 to 40 mils (0.127 to 1.016 mm)) may be utilised. Yarns of 20 to 200 continuous filaments are commonly formed. The melt-spinnable poly(ester-amide) is supplied to the extrusion orifice at a temperature above its melting temperature, e.g., a temperature of 270°C to 330°C. in preferred embodiments.

Subsequent to extrusion through the shaped orifice, the resulting filamentary material or film is passed in the direction of its length through a solidification or quench zone wherein the molten filamentary material or film is transformed into a solid filamentary material or film. The resulting fibres commonly have a denier per filament of 2 to 40, and preferably a denier per filament of 3 to 5.

The resulting filamentary material or film optionally may be subjected to a thermal treatment whereby its physical properties are further enhanced. The tenacity of the fibre or film generally is increased by such thermal treatment. More specifically, the fibres or films preferably may be thermally treated in an inert atmosphere (e.g., nitrogen, argon, helium) or alternatively in a flowing oxygen-containing atmosphere (e.g., air) with or without stress at a temperature below the polymer melting temperature until the desired property enhancement is achieved. Thermal treatment times commonly range from a few minutes to several days. Generally, as the product is thermally treated, its melting temperature progressively is raised. The temperature of the atmosphere may be staged or continuously increased during the thermal treatment or held at a constant level. For instance, the product may be heated at 250°C. for one hour, at 260°C. for one hour and at 270°C. for one hour. Alternatively, the product may be heated at 10°C. to 20°C. below the temperature at which it melts for about 45 hours. Optimal heat treatment conditions will vary with the specific composition of the poly(ester-amide) and with the process history of the product.



The as-spun fibres formed from the poly(ester-amide) of the present invention are fully oriented and exhibit highly satisfactory physical properties which render them suitable for use in high performance applications. The as-spun fibres commonly exhibit an average single filament tenacity of at least 1 gram per denier (e.g., 3 to 10 grams per denier) and an average single filament tensile modulus of at least 200 grams per denier (e.g., 300 to 800 grams per denier) and exhibit an extraordinary dimensional stability at elevated temperature (e.g., at temperatures of 150 to 200°C.). Following thermal treatment (i.e., annealing), the fibres commonly exhibit an average single filament tenacity of at least 5 grams per denier (e.g., 15 to 40 grams per denier). Such properties enable the fibres to be used with particular advantage as tyre cords and in other industrial application, such as conveyor belts, hose, rope, cabling, resin reinforcement, etc. Films formed of the poly(ester-amide) of the present invention may be used as strapping tape, cable wrap, magnetic tape, electric motor dielectric film, etc. The fibres and films exhibit an inherent resistance to burning.

It is anticipated that the poly(ester-amide) compositions of the present invention will exhibit improved adhesion, improved fatigue resistance and increased transverse strength over known polymers, such as wholly aromatic polyesters.

The following Examples are presented as specific illustrations of the claimed invention. It should be understood, however, that the invention is not limited to the specific details as set forth in the Examples.



EXAMPLE 1

This Example illustrates the preparation of a poly (ester-amide) from 6-hydroxy-2-naphthoic acid, p-amino-benzoic acid, and p-hydroxybenzoic acid (or derivatives thereof) in the molar ratio 60:20:20.

5        A 300 ml. 3-neck polymer flask was fitted with a sealed glass paddle stirrer, a gas inlet, and a distillation head and condenser. Into the flask were placed 69.0 g. (0.3 mole) of 6-acetoxy-2-naphthoic acid, 17.9 g. (0.1 mole) of p-acetamidobenzoic acid, and 18.0 g. (0.1 mole) of p-acetoxybenzoic acid. No catalyst was added. The flask was  
10        evacuated and flushed with nitrogen three times. The flask was heated in an oil bath to 250°C. under a slow stream of nitrogen gas. The contents rapidly melted to an opaque slurry and agitation was begun. Acetic acid rapidly began  
15        to distil over and was collected in a graduated cylinder. After only 8 minutes at 250°C., 12 ml (42% of the theoretical yield) of acetic acid had been collected, and the melt was foaming vigorously. Heating and stirring were continued for 45 minutes, by which time a total of 21 ml. (73% of the  
20        theoretical yield) of acetic acid had been collected. The temperature was raised to 280°C. and held there for 30 minutes. Initially, the melt became foamy again, but the foaming subsided as the viscosity increased. At the end of this period, a total of 24.5 ml. (86% of the theoretical  
25        yield) of acetic acid had been collected, and the temperature was raised to 320°C. The melt was held at this temperature for an additional 10 minutes, at the end of which time the total yield of acetic acid was 25 ml. (90% of theoretical). Vacuum (0.6 mm. Hg) was then slowly applied in order to  
30        minimize foaming. The melt was heated under full vacuum for 20 minutes, and the temperature was slowly raised to 340°C. The opaque melt was very viscous.

At the end of the heating cycle, the vacuum was released with nitrogen, and the flask was allowed to cool  
35        under a nitrogen atmosphere. When cool, the flask was broken and the polymer was freed from broken glass and ground in a Wiley mill. The powdered polymer was extracted

in a Soxhlet apparatus with acetone to remove low molecular weight impurities and was then dried overnight in a vacuum oven.

The polymer exhibited an inherent viscosity of 2.27  
5 dl./g. when measured at a concentration of 0.1 weight/volume percent in pentafluorophenol at 60°C. The polymer exhibited a glass-rubber transition inflection at 102°C. and a  $T_m$  endotherm at 277°C. when measured by differential scanning calorimetry. When the polymer was examined under a micro-  
10 scope utilizing crossed polarizers, an anisotropic melt was observed above approximately 285°C.

The polymer was melt spun through a 0.007 inch (0.178 mm) single hole jet at 300°C. at a throughput of 0.14 g./min. and at a take-up speed of 184 m./min. The single filament  
15 properties of the as-spun fiber were:

Tenacity	2.84 g./d.
Elongation	1.3%
Initial Modulus	276 g./d.
Denier	20

20

#### EXAMPLE 2

This Example illustrates the preparation of a poly (ester-amide) from 6-hydroxy-2-naphthoic acid, p-methyl-aminobenzoic acid, and p-hydroxybenzoic acid (or derivatives thereof) in the ratio 60:20:20.

25 The apparatus used was identical to that used in Example 1. Into the flask were placed 69.0 g. (0.3 mole) of 6-acetoxy-2-naphthoic acid, 19.3 g. (0.1 mole) of p-(N-methyl) acetamidobenzoic acid, and 18.0 g. (0.1 mole) of p-acetoxybenzoic acid.

30 The flask was evacuated and flushed with nitrogen three times. The flask was heated at 250°C. in an oil bath. Initially, the melt was a clear brown color, but as the reaction proceeded, it rapidly became opaque as acetic acid distilled over. After 45 minutes, a total of 14 ml. (50%  
35 of theoretical yield) of acetic acid had been collected. The temperature was raised to 280°C. The melt became foamy, and the rate of agitation was increased until the foaming had subsided. After 45 minutes at 280°C., a total of 23.8 ml.

(83% of theoretical) of acetic acid had been collected.

The temperature was raised to 320°C. and was held there for an additional 45 minutes. At the end of this time, the melt was quite viscous, and a total of 26.2 ml. (92% of the  
5 theoretical yield) of acetic acid had been collected. The melt was raised to 340°C. for 25 minutes. Vacuum (0.6 mm. Hg) was applied for 20 minutes. The melt balled up around the stirrer shaft.

The flask was cooled under a nitrogen atmosphere, and  
10 the polymer was isolated and ground as before. The polymer exhibited an inherent viscosity of 1.59 dl./g. when measured at a concentration of 0.1 weight/volume percent in penta-fluorophenol at 60°C. The polymer exhibited a well-defined endotherm at 295°C. when measured by differential scanning  
15 calorimetry. When the polymer was examined under a microscope utilizing crossed polarizers, an anisotropic melt was observed above approximately 300°C.

The polymer was melt spun through a 0.007 inch (0.178 mm) single hole jet at 330°C. at a throughput of 0.42 g./min.  
20 and at a take-up speed of 321 m./min. The single filament properties of the as-spun fiber were:

	Tenacity	8.0 g./d.
	Elongation	2.3%
	Initial Modulus	498 g./d.
25	Denier	12.6

A sample was heat treated for 15 hours at 285°C. in a nitrogen atmosphere. The properties of the heat treated fiber were:

	Tenacity	17.0 g./d.
30	Elongation	4.3%
	Initial Modulus	530 g./d.

#### EXAMPLE 3

The poly(ester-amide) described in Example 1 was again prepared under virtually identical conditions except that  
35 the vacuum cycle time was extended to 40 minutes while the temperature increased from 320°C. to 340°C. The product exhibited an inherent viscosity of 4.81 dl./g. when measured at a concentration of 0.1 weight/volume percent in

pentafluorophenol at 60°C. An anisotropic melt was observed above 300°C. when the polymer was examined under a microscope utilizing crossed polarizers.

The polymer was ground in a mill and melt spun through a single 0.007 inch (0.178 mm) hole at 376°C. at a throughput of 0.14 g./min. and at a take-up speed of 40 m./min. The single filament properties of the as-spun fiber were:

	Tenacity	6.3 g./d.
10	Elongation	1.6%
	Initial Modulus	490 g./d.
	Denier	31.4

#### EXAMPLE 4

This Example illustrates the preparation of a poly (ester-amide) from 6-hydroxy-2-naphthoic acid, p-methyl-aminobenzoic acid, and p-hydroxybenzoic acid (or derivatives thereof) in the molar ratio 60:30:10.

As in Example 1, the reaction flask was charged with 69.0 g. (0.3 mole) of 6-acetoxy-2-naphthoic acid, 29.0 g. (0.15 mole) of 4-(N-methyl)acetamidobenzoic acid, and 9.0 g. (0.05 mole) of 4-acetoxybenzoic acid.

The polymerization was carried out under the same time and temperature conditions as in Example 2, except that the final vacuum cycle lasted 32 minutes, the temperature being steadily raised from 320°C. at the start to 340°C. at the end. The pale tan opaque melt had a "pearly" appearance and upon solidification had a "woody" fracture.

After isolation and grinding, the polymer exhibited an inherent viscosity of 1.03 dl./g. when measured at a concentration of 0.1 weight/volume percent in pentafluorophenol at 60°C. The polymer exhibited a glass-rubber transition inflection at 110°C. and a  $T_m$  endotherm at 310°C. when measured by differential scanning calorimetry. When the polymer was examined under a microscope utilizing crossed polarizers, an anisotropic melt was observed above 320°C.

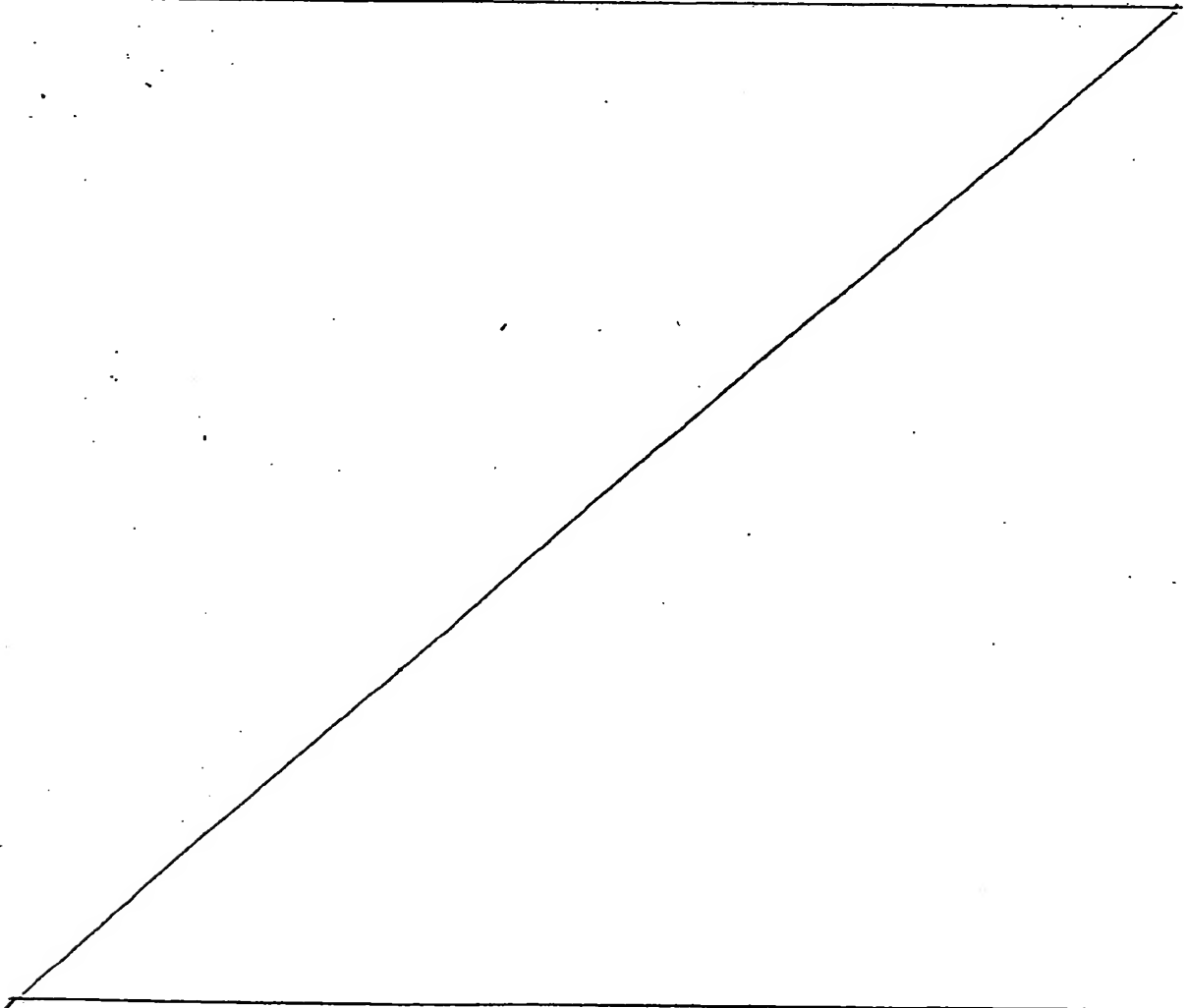
The polymer was melt spun through a 0.007 inch (0.178 mm) single hole jet at 360°C. at a throughput of 0.42 g./min. and at a take-up speed of 199 m./min. The single filament properties of the as-spun fiber were:

Tenacity	6.7 g./d.
Elongation	2.1%
Initial Modulus	431 g./d.
Denier	23.7

The fiber was heat treated at 300°C. for eight hours in a nitrogen atmosphere. The heat treated fiber exhibited the following properties:

Tenacity	14.3 g./d.
Elongation	3.4%
Initial Modulus	481 g./d.

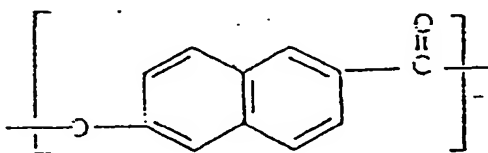
Although the invention has been described with preferred embodiments, it is to be understood that variations and modifications may be employed as will be apparent to those of ordinary skill in the art. Such variations and modifications are to be considered within the purview and scope of the claims appended hereto.



CLAIMS

1. A melt processable poly(ester-amide) capable of forming an anisotropic melt phase at a temperature below 400°C. consisting essentially of recurring moieties I, II and (optionally) III wherein:

I is



II is  $\left[ \text{Z}-\text{Ar}-\overset{\text{O}}{\underset{\parallel}{\text{C}}} \right]_n$

where Ar is a divalent radical comprising at least one aromatic ring, and Z is NH or NR (where R is an alkyl group of 1 to 6 carbon atoms or an aryl group); and

III is  $\left[ \text{O}-\text{Ar}'-\overset{\text{O}}{\underset{\parallel}{\text{C}}} \right]_n$

where Ar' is a divalent radical comprising at least one aromatic ring other than naphthylene;

wherein at least some of the hydrogen atoms present upon any of the rings of the various moieties may optionally be replaced by substituents selected from alkyl groups of 1 to 4 carbon atoms, alkoxy groups of 1 to 4 carbon atoms, halogen, phenyl and mixtures thereof,

and wherein moiety I is present in a concentration of 10 to 90 mole percent, moiety II is present in a concentration of 5 to 45 mole percent, and moiety III is present in a concentration of 0 to 45 mole percent, the total concentration of moieties I and III being from 55 to 95 mole percent.

2. The poly(ester-amide) of claim 1 which is capable of forming an anisotropic melt phase at a temperature below 350°C.

3. The poly(ester-amide) of claim 1 or 2 which exhibits an inherent viscosity of at least 1.0 dl./g. when measured at a concentration of 0.1 weight/volume percent in pentafluorophenol at 60°C.



4. The poly(ester-amide) of claim 3 which exhibits an inherent viscosity of at least 2.0 dl./g. when measured at a concentration of 0.1 weight/volume percent in pentafluorophenol at 60°C.
5. The poly(ester-amide) of any of claims 1 - 4 wherein moiety I is present in a concentration of 20 to 80 mole percent.
6. The poly(ester-amide) of claim 5 wherein moiety I is present in a concentration of 30 to 70 mole percent.
7. The poly(ester-amide) of any of claims 1 - 6 wherein moiety II is present in a concentration of 5 to 35 mole percent.
8. The poly(ester-amide) of claim 7 wherein moiety II is present in a concentration of 10 to 30 mole percent.
9. The poly(ester-amide) of any of claims 1 - 8 wherein moiety III is present in a concentration of at least 5 mole percent.
10. The poly(ester-amide) of claim 9 wherein moiety III is present in a concentration of at least 10 mole percent.
11. The poly(ester-amide) of claim 10 wherein moiety III is present in a concentration of 10 to 30 mole percent.
12. The poly(ester-amide) of any of claims 1 - 9 wherein the total concentration of moieties I and III is from 65 to 95 mole percent.
13. The poly(ester-amide) of claim 12 wherein the total concentration of moieties I and III is from 70 to 90 mole percent.
14. The poly(ester-amide) of any of claims 1 - 13 wherein moiety II is derived from p-aminobenzoic acid.
15. The poly(ester-amide) of any of claims 1 - 14 wherein moiety III is a p-oxybenzoyl moiety.
16. A moulding compound comprising the melt processable poly(ester-amide) of any of claims 1 - 15 which incorporates 1 to 60 percent by weight of a solid filler and/or reinforcing agent.
17. A moulded article comprising the melt processable poly(ester-amide) of any of claims 1 - 15 or the moulding compound of claim 16.



18. A fibre which has been melt spun from the poly(ester-amide) of any of claims 1 - 15.
19. A film which has been melt extruded from the poly(ester-amide) of any of claims 1 - 15.

BAD ORIGINAL



European Patent  
Office

## EUROPEAN SEARCH REPORT

0063880

Application number

EP 82 30 1812

DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl. 3)
	"No relevant documents have been disclosed" -----		C 08 G 69/44
			TECHNICAL FIELDS SEARCHED (Int. Cl. 3)
			C 08 G 69
The present search report has been drawn up for all claims			
Place of search THE HAGUE		Date of completion of the search 14-06-1982	Examiner LEROY ALAIN
<b>CATEGORY OF CITED DOCUMENTS</b>			
X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document		T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons & : member of the same patent family, corresponding document	

EPO Form 1503 03.82



**This Page is Inserted by IFW Indexing and Scanning  
Operations and is not part of the Official Record**

**BEST AVAILABLE IMAGES**

Defective images within this document are accurate representations of the original documents submitted by the applicant.

Defects in the images include but are not limited to the items checked:

- ☐ **BLACK BORDERS**
- ☐ **IMAGE CUT OFF AT TOP, BOTTOM OR SIDES**
- ☐ **FADED TEXT OR DRAWING**
- ☐ **BLURRED OR ILLEGIBLE TEXT OR DRAWING**
- ☐ **SKEWED/SLANTED IMAGES**
- ☐ **COLOR OR BLACK AND WHITE PHOTOGRAPHS**
- ☐ **GRAY SCALE DOCUMENTS**
- ☐ **LINES OR MARKS ON ORIGINAL DOCUMENT**
- ☐ **REFERENCE(S) OR EXHIBIT(S) SUBMITTED ARE POOR QUALITY**
- ☐ **OTHER: \_\_\_\_\_**

**IMAGES ARE BEST AVAILABLE COPY.**

**As rescanning these documents will not correct the image problems checked, please do not report these problems to the IFW Image Problem Mailbox.**